Thermochemical Models and Databases for High-Temperature Materials Processing and Corrosion

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Industrial Materials of the Future Team

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Thermochemical data are an essential part of understanding any high-temperature process

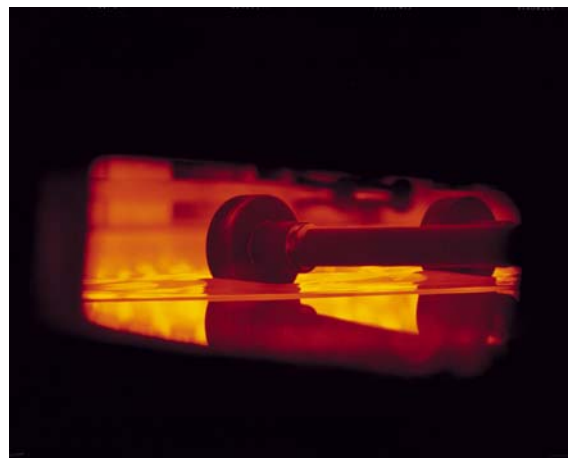
Project Objectives

- To provide thermochemical data and models for an important set of industrial materials - refractories and glasses
- To incorporate this data into a comprehensive web-based tool

Project Benefits

- Improved energy utilization
- Reduced corrosion
- Reduced waste; more efficient use of raw materials
- Reduced emissions

Systems included in the database are selected for their relevance to problems in the OIT Industries of the Future and through critical assessment of the available data



Project Tasks / Participants

Tasks:

1. **Thermodynamic modeling of condensed-phase systems**
   - Ted Besmann, ORNL
   - Nagraj Kulkarni, ORNL
2. **Prediction of high-temperature thermochemistry of gas-phase systems**
   - Mark Allendorf, SNL
   - Ida Beck Nielsen, SNL
   - Carl Melius, LLNL
3. **Web site development**
   - Mark Allendorf, SNL
   - Michelle Medlin, SNL

- **Advisory committee**
  - Dr. Ovidu Marin, Air Liquide
  - Dr. David Russo, Atofina
  - Dr. Randy John, Shell Oil
  - Dr. John Connors, PPG Industries
  - Dr. David Strickler, Pilkington-LOF
  - Dr. Amul Gupta, Monafrax
  - Dr. Dilip Patel, RHI Refractories
  - Dr. Angel Sanjurjo, SRI International
  - Dr. Ellen Meeks, Reaction Design

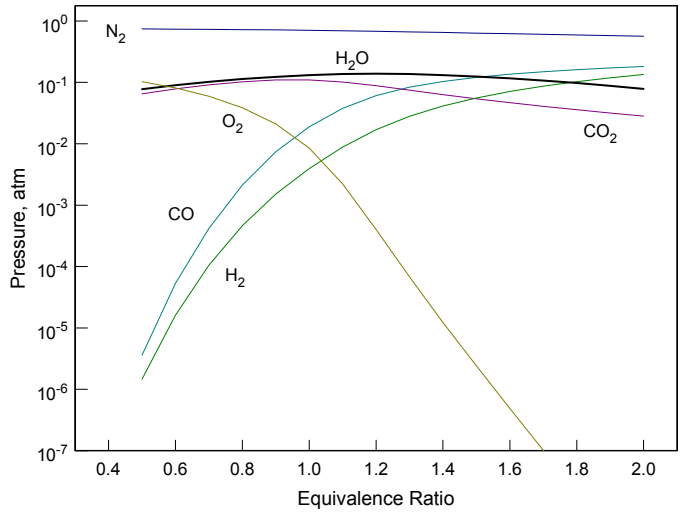
Program plan/ Milestone status

Milestone Plan

- **Year 2**
  - **Develop, validate subcomponents for condensed-phase model Complete**
  - **Complete expansion of main-group gas-phase thermochemistry to include In, Sn, Sb On track to complete by 9/30/03**
  - **Initiate model development for prediction of transition-metal thermochemistry method development slated to begin 7/1/03**
- **Year 2.5**
  - **Make decision on ability to build comprehensive condensed-phase thermochemical model Decision to proceed; model successfully demonstrated**
- **Year 3**
  - **Develop software to convert CHEMKIN thermodynamic fits to ChemSage/FACTSage format**
  - **Complete basic web page design Complete**
- **Year 4**
  - **Complete integrated web-based thermochemical information system**
- **Year 5**
  - **Complete transfer of existing gas-phase data (> 3,000 species) approximately 700 species transferred to date**

Industrial environments often contain an aggressive combination of corrosive gases and high temperatures

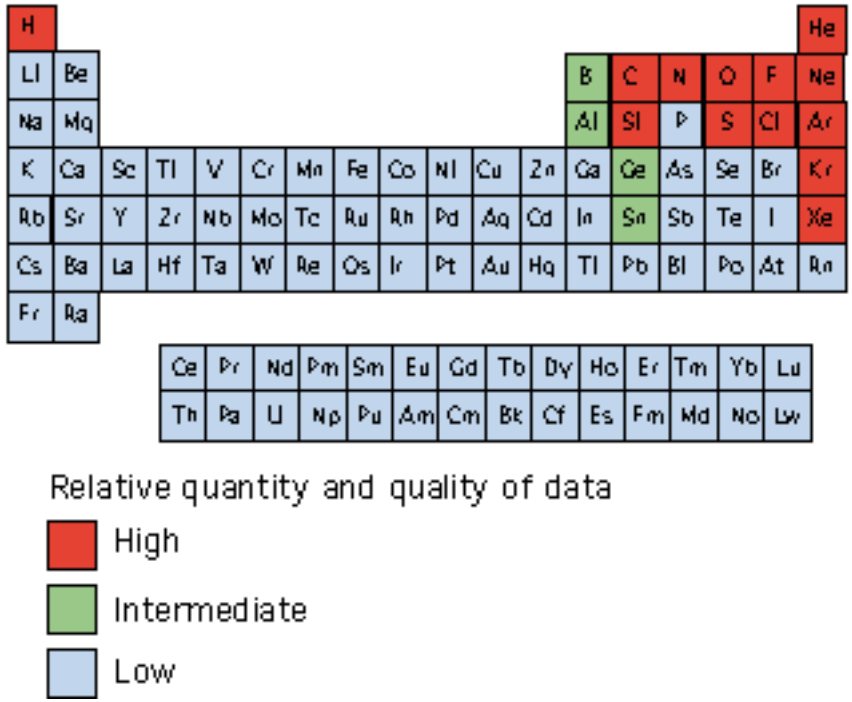
- Combustion (virtually all industries)
  - Products always contain ~10% water vapor
- Glass making
  - T > 1100 °C for refractories
  - High NaOH, KOH, boron species, Pb
  - Glass/refractory contact
  - Chlorine compounds (from coating operations)
- Pulp and paper black liquor combustion or gasification
  - Very high alkali
  - Chlorine
- Metals production
  - molten-metal/refractory contact



This leads to serious materials problems that often limit facility lifetimes

Thermochemical data are of fundamental importance to controlling high-temperature processes

- **Basis for determining potential for chemical reaction of materials at high temperature**
  - **Thermal stability**
  - **Corrosion**
  - **Material synthesis**
- **Decline in research efforts over past two decades**
  - **Standard data bases incomplete or out of date**
  - **No significant ongoing experimental efforts**
- ***But - there are increasing needs for:***
  - **Materials stable in harsher environments**
  - **New engineered materials**
- **Data needed (25 - 2700 °C)**
  - **Self-consistent data for solid solutions**
  - **Gas-phase data, esp. for non-combustion chemistries**
  - **Heats of formation**
  - **Entropies**
  - **Heat capacities**

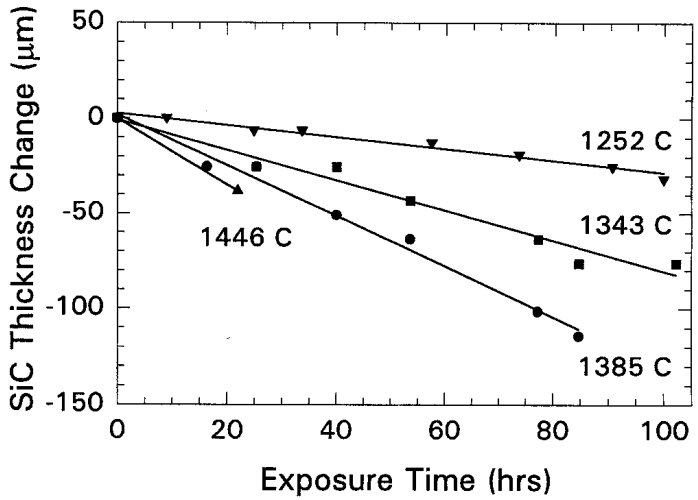


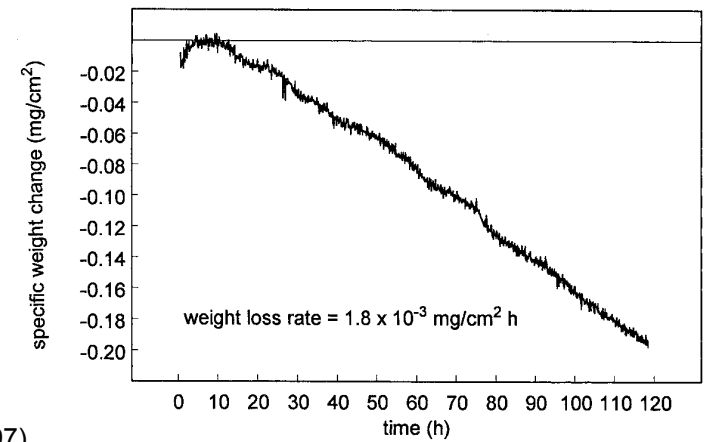
Computational methods are the only option for obtaining these crucial data

Corrosion of silicon-based ceramics by water vapor at combustion temperatures is well documented

- **Silicon carbide (used in gas turbines)**
  - $SiC + 3/2\ O_2(g) = SiO_2 + CO(g)$
  - $SiO_2 + 2\ H_2O(g) = Si(OH)_4(g)$
- **Silica (used in the glass industry)**
  - $SiO_2 + 2\ H_2O(g) = Si(OH)_4(g)$

Robinson, Smialek, Opila, et al. *J. Am. Ceram. Soc* 82, 1817 (1999).

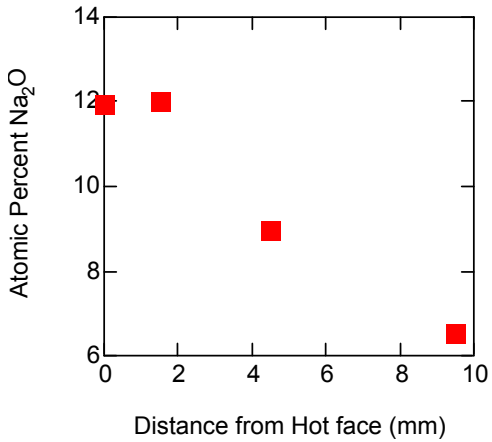


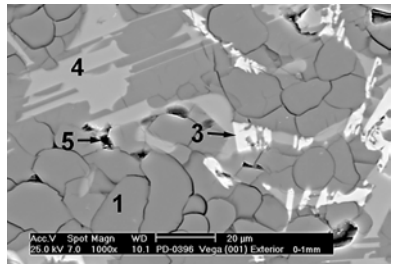


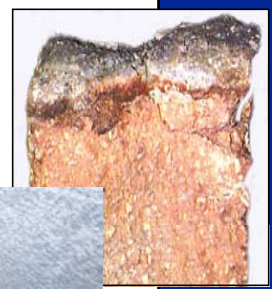
Opila and Hann, *J. Am. Ceram. Soc.* 80, 197 (1997).

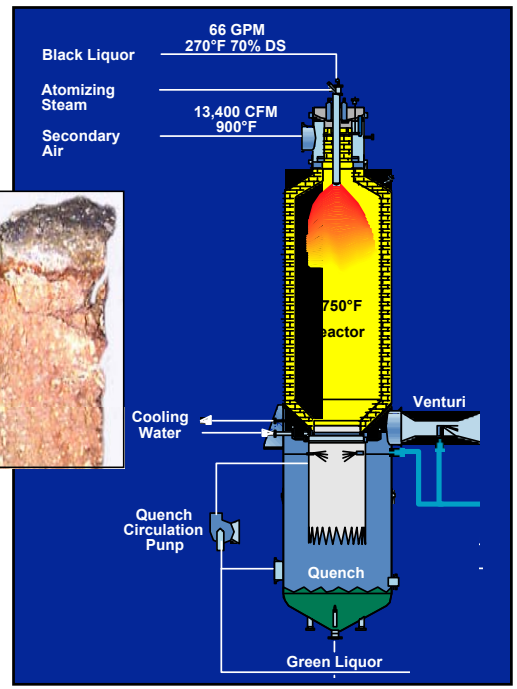
Alkali corrosion of refractories can severely limit furnace lifetimes

- **Black-liquor gasifiers – e.g., New Bern gasifier problems**
  - Mullite-based refractory lining degraded rapidly
  - Alumina-based replacement refractory degraded more rapidly than expected
  - Successful gasifiers can improve efficiency of mill power production and use of biomass fuels or black liquor
- **Oxy-fuel glass furnaces**
  - Corrosion rate of standard low-density silica refractory 2X higher in high-oxygen environments
  - Oxy/fuel melting is 20-40% more energy efficient than air/fuel



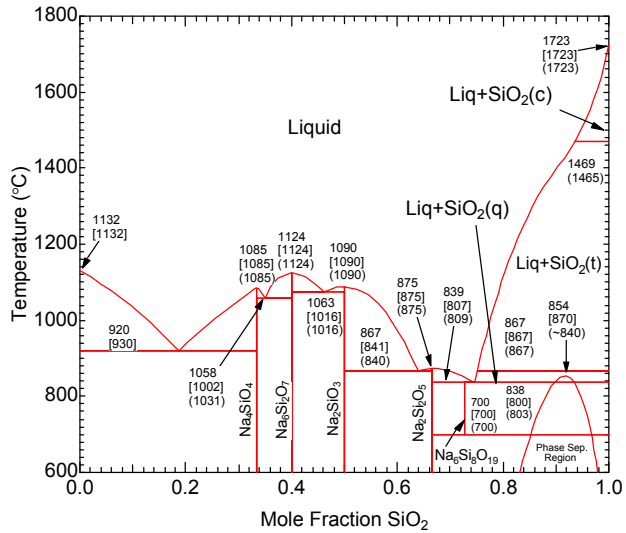






Modeling the thermochemistry of glass melts is particularly difficult

- **Large number of oxide components**
  - **Si, Na, K, Mg, Ca**
  - **B, Al, Sb, Pb**
  - **Ti, Fe, Zr**
  - **Sulfur**
- **Strong interactions among components, leading to non-ideal-solution behavior**
- **Need accurate thermochemistry to predict:**
  - **New glass compositions (lighter, higher-strength glass saves energy in manufacturing)**
  - **Interactions with containment refractories**
  - **Production of particulates and other emissions**



Task 1: Objectives

- **Develop practical models for calculating thermodynamic stabilities of components in complex oxides and glasses of value to design and use of refractories, glass manufacturing**
  - **Allow a large number of species/phases to be used**
  - **Make the model easy to understand and use**
  - **Base results on established phase-diagram data so it's reliable**
  - **Design for easy extension to other (T, x_i) regimes via interpolation or extrapolation**

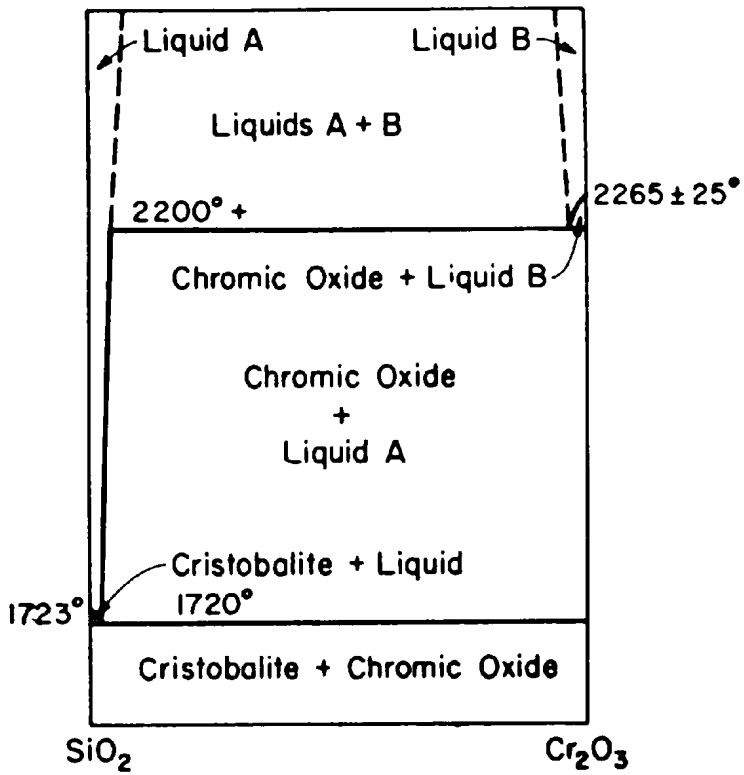
The modified associate species model is being used to predict thermochemistry for condensed-phase species in the database

Summary - Task 1

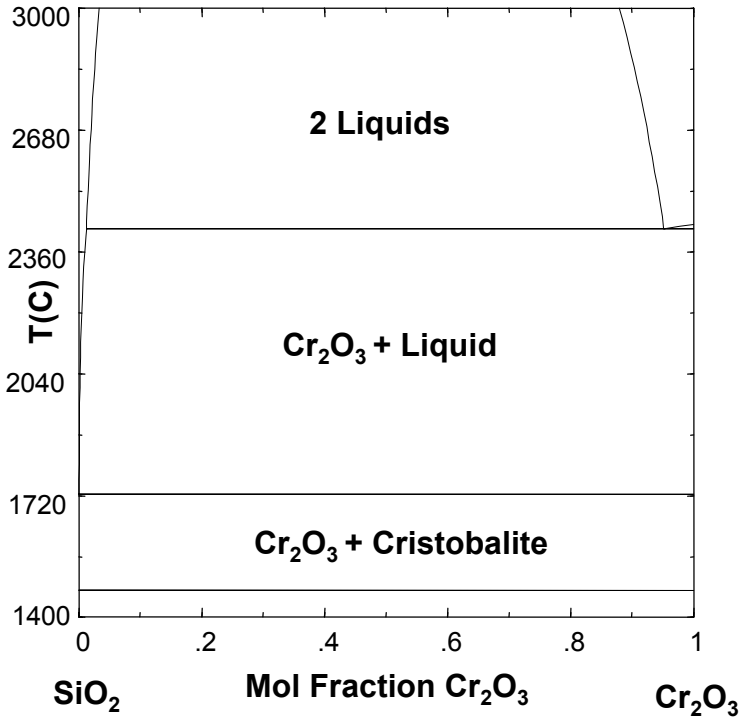
- Representative glass constituents are being used in the development of a thermochemical model based on the modified associate species approach
- Optimized subsystems accurately represent observed phase equilibria
- A global model for the Na_2O-Al_2O_3-Cr_2O_3-MnO-NiO-B_2O_3-SiO_2 system has been made operational
- The model was used to compute the effects of chromia content liquidus

The Cr_2O_3-SiO_2 Was Modeled With Positive Interaction Parameters to Reproduce Experimental Diagram

Published (No. 332)

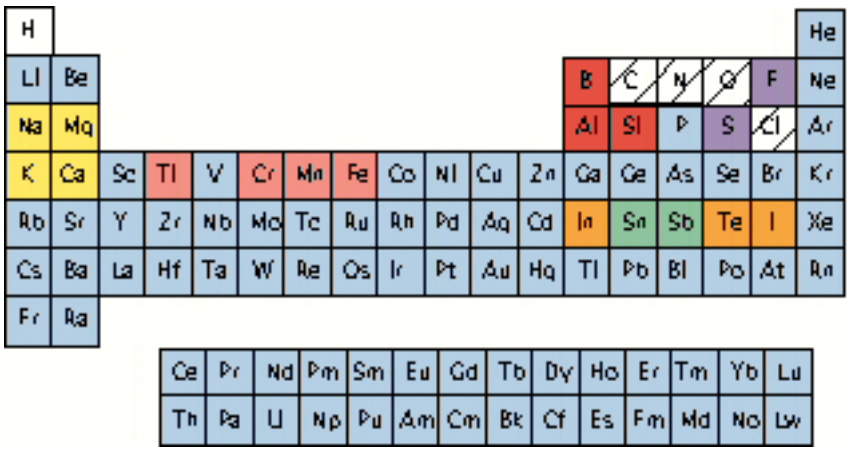


Computed Phase Diagram



The computed diagram reflects the newer melting point of Cr_2O_3 of 2330°C

Task 2: Status of gas-phase database - Year 2 activities



- **Principal quantum-chemistry methods used:**
  - **Bond Additivity Correction method**
  - **Coupled Cluster Theory**
- **New thermochemistry**
  - **86 Sn-H-C-Cl compounds complete**
  - **Data for Sb and In slated for completion by 9/30/03**
- **Method development**
  - **Half-time staff member dedicated to method development**
  - **BAC-MP4 for In, Sn, Sb complete (9/30)**
  - **New coupled-cluster BAC method for oxides**
  - **Transition metal model development begins this project year, initially focussing on Ti, Cr, Mn, Fe**

H	Complete	F	Data available but not uploaded
C	Partially uploaded dataset	Sn	New method and data
B	Newly added data	In	Method under development
Na	Data available elsewhere	Tl	New elements for PY3

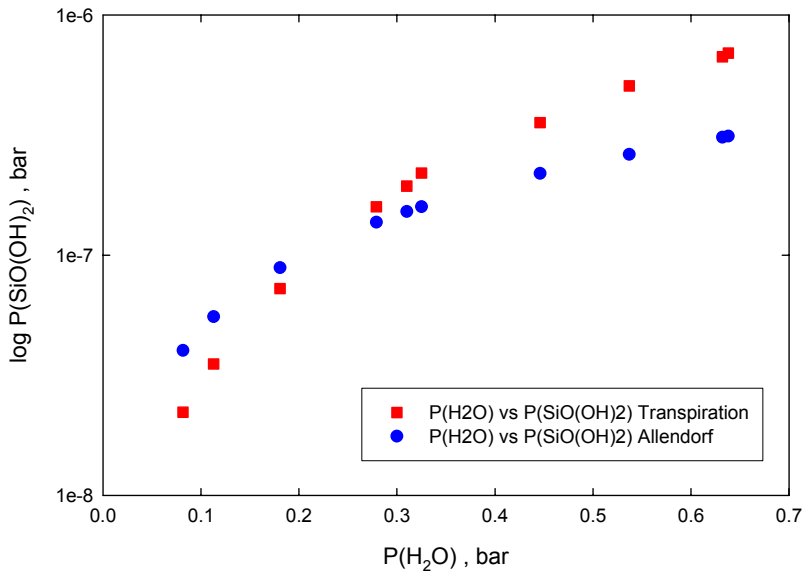
New experimental results are in excellent agreement with BAC-MP4 predictions for silicon hydroxides

Heat of reaction:

$SiO_2(cr) + H_2O(g) = Si(OH)_4(g)$

Study	T(K)	$\Delta_r H$ (kJ/mol)	$\Delta_r S$ (J/mol-K)
Second law Hashimoto (1992)	1600	56.7 ± 1.7	-66.2 ± 1.0
2nd law Jacobson et al	1200	54.6 ± 2.7	-67.5 ± 2.1
3rd law Jacobson et al	298.15	58.4 ± 3.6	
Ab-initio Allendorf et al.	298.15	55.3	
Estimate from psuedo-halide behavior (Krikorian)	298.15	56.5	

Transpiration Measurements for $SiO(OH)_2$ at 1673 K



Comparison of experiment with theory for $SiO(OH)_2$ at 1673 K

Data from Jacobson et al. NASA/Lewis Research Center, 2003

Task 3: Database/Website development - Year 2 activities

Site is open to the public! Data are available at NO CHARGE!

www.ca.sandia.gov/HiTempThermo/index.html

Condensed-phase data:

- **Extensive data set for important industrial materials systems:**
  - **SiO_2/Na_2O/K_2O (glass manufacturing)**
  - **Na_2O-Al_2O_3-Cr_2O_3-B_2O_3-SiO_2 system available for modeling chromia-containing systems, including corrosion of chromia refractories**
  - **Global Na_2O-Al_2O_3-Cr_2O_3-MnO-NiO-B_2O_3-SiO_2 system uploaded to website for modeling complex glasses, refractories, alloy corrosion products, etc.**

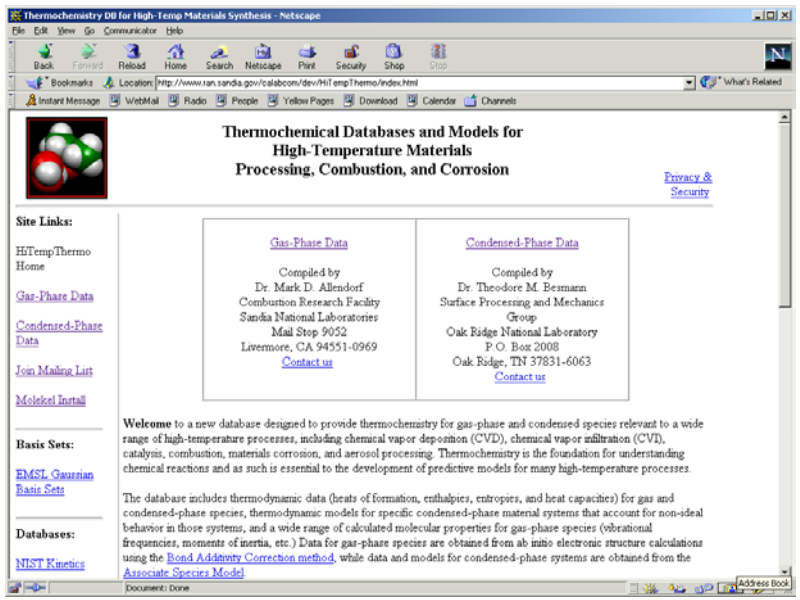
Gas-phase data:

- **New gas-phase thermochemistry**
  - **> 400 C-H-O species relevant to natural-gas combustion**
  - **120 B-H-C-N-O-Si-Cl (B-O-H data completely new)**
  - **66 Al-C-N-O-F-Cl species**
  - **> 200 Si-H-C-N-O-F-Cl (partially complete)**
  - **Sn-H-C-Cl compounds uploaded by 9/30/03**

Our data are well documented with a clear pedigree, unlike most commercial (encrypted) databases

Site enhancements and management

- **Subcontract placed to retain Michelle Medlin as site manager**
- **Numerous features and upgrades to site structure, including:**
  - **Error estimates**
  - **Shopping cart to facilitate downloading of data**
  - **Improved search engine on line later this year**
  - **Expanded links to relevant sites**
  - **3D molecule viewer**
  - **Mailing list**



Feedback from users provides useful insight into improvements and needed data

- Industry advisory group
  - Survey issued to obtain feedback from this group
  - Several useful comments concerning web design

- On-line user community
  - Users may “subscribe” - 54 to date
  - Provides ability to keep community informed of developments and changes in the database
  - User-provided suggestions are being incorporated into the site

Getting the word out

- **Links to other web sites:**
  - Materials Research Society
  - American Ceramic Society
  - The Electrochemical Society
  - Reaction Design Inc. (supplier of software to the chemicals and combustion industries)
  - International Combustion Institute (under consideration)
- **Publications and presentations**
  - Article in *Combustion Research Facility News* (> 1600 subscribers)
  - Article in *Refractories Applications and News*
  - Article in *IMF Highlights*, spring 2003
  - Announcement by Glass Manufacturer Industry Council (GMIC)
  - Presentations at technical conferences:
    - American Ceramic Society
    - 4th International Conference on Coatings on Glass
    - 16th International Conference on Chemical Vapor Deposition
    - High Temperature Materials Gordon Conference
    - DOE/OIT Glass Industry of the Future Program Review

Plans for FY04

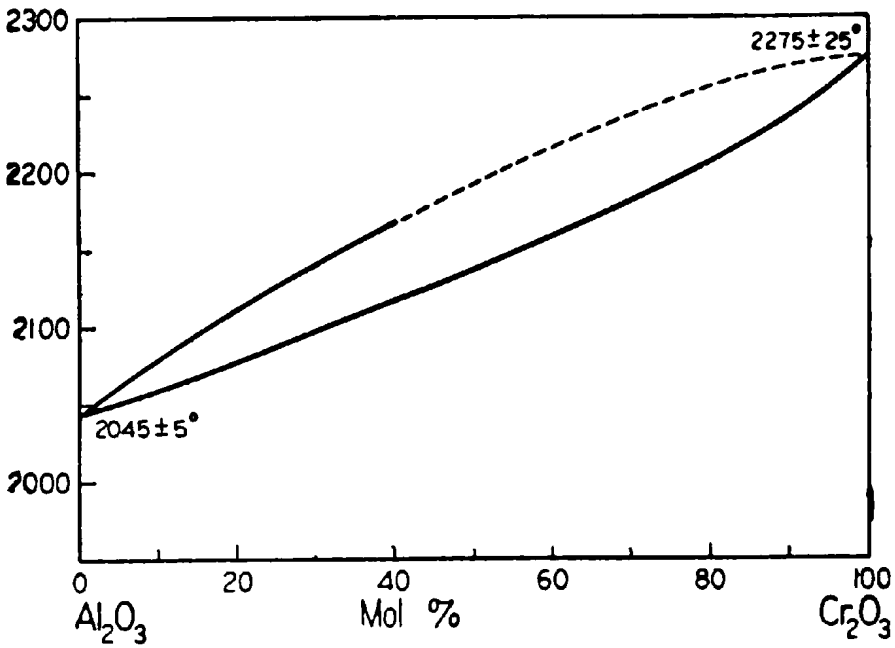
- Task 1
  - Expand condensed phase model/database to include calcia, zirconia, iron oxides, and sulfur and phosphorus
  - Develop flexible model for crystalline, complex spinels for use in global model
- Task 2
  - Establish approach to prediction of gas-phase transition-metal thermo for first-row compounds (primarily Ti, Cr, Mn, Fe)
  - Expand data relevant to combustion processes
- Task 3
  - Develop software to convert CHEMKIN thermodynamic fits to FACTSage format
  - Complete web design
  - Upload remaining inorganic main-group data

FactSage Demonstration

Backup slides

Modeling the Cr_2O_3-Al_2O_3 System Is Challenging Due to the Solid Solutions and 2-Solution Phase Regions

Published (No. 309)



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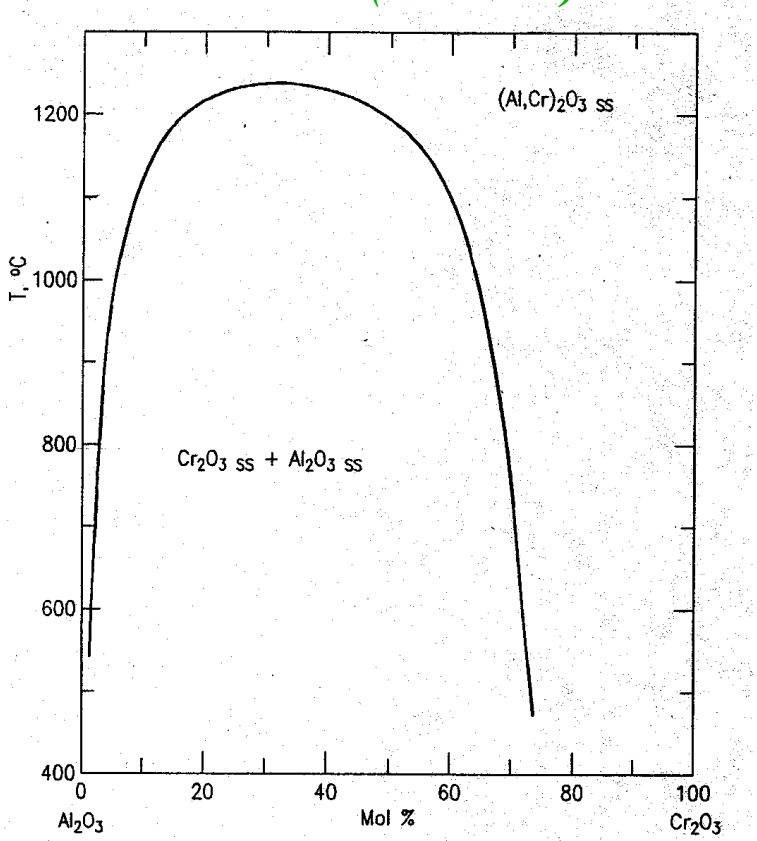
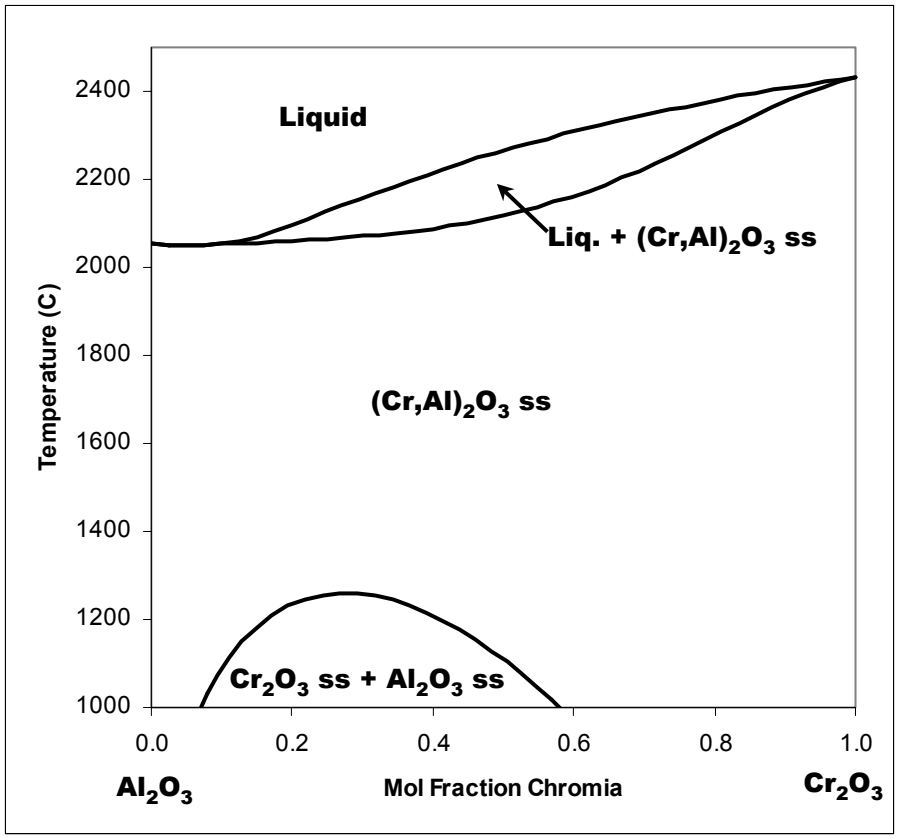


Computed Phase Diagram for the Cr_2O_3-Al_2O_3 System

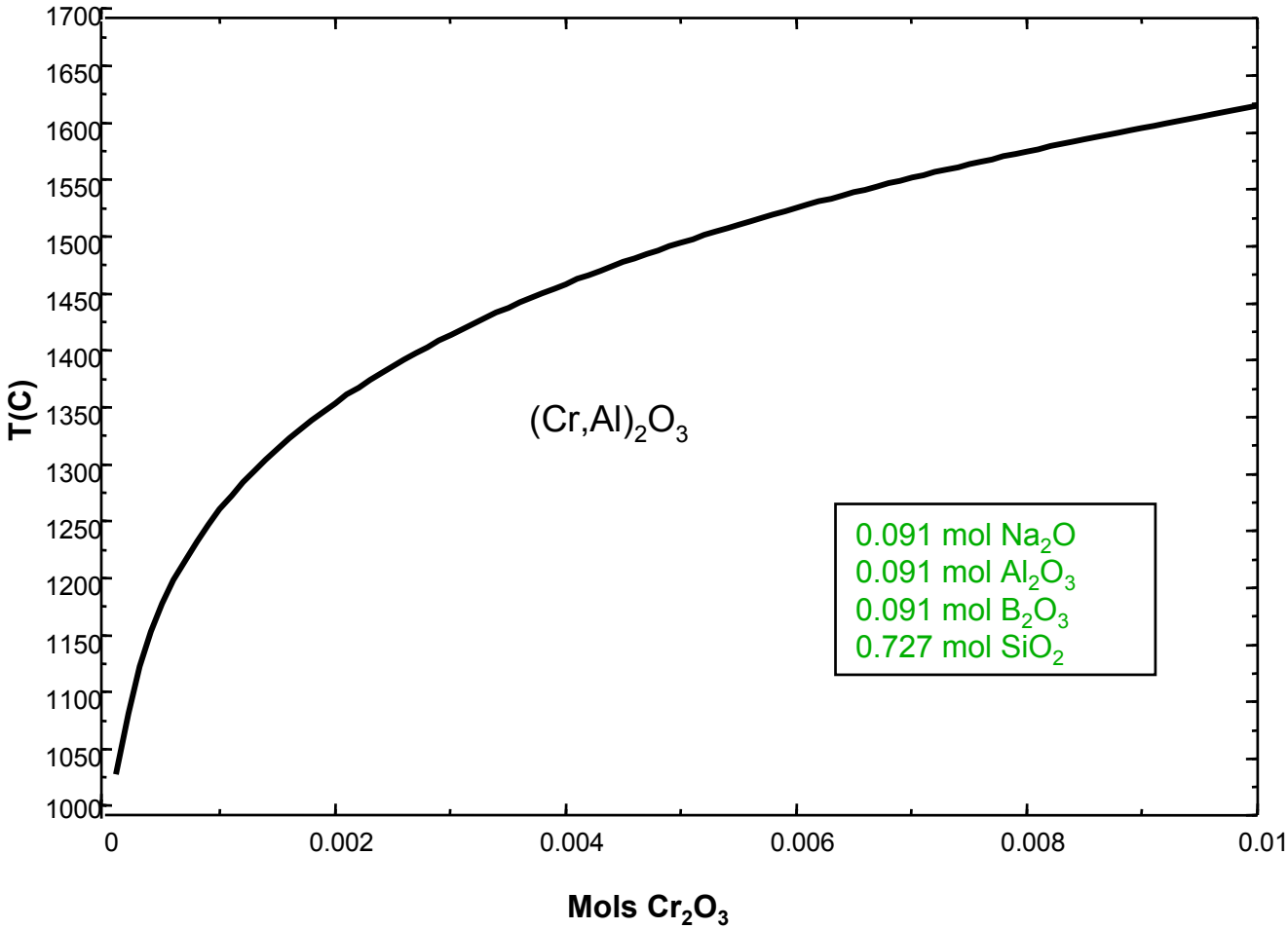


- Liquid treated as ideal solution of end member liquids
- Corundum treated as solution of:
  - Cr_2O_3
  - Al_2O_3
- With interaction energies

$$G_{ex} = X(1-X)[(26{,}500-7T)+(1-2X)(-12{,}000)$$

where X is the mol fraction of Al_2O_3

Liquidus Curve for the Na_2O-Cr_2O_3-Al_2O_3-B_2O_3-SiO_2 System Strongly Affected by Cr_2O_3 Content



Published and Computed Phase Diagrams for Al_2O_3-MnO and MnO-SiO_2 Show Good Agreement

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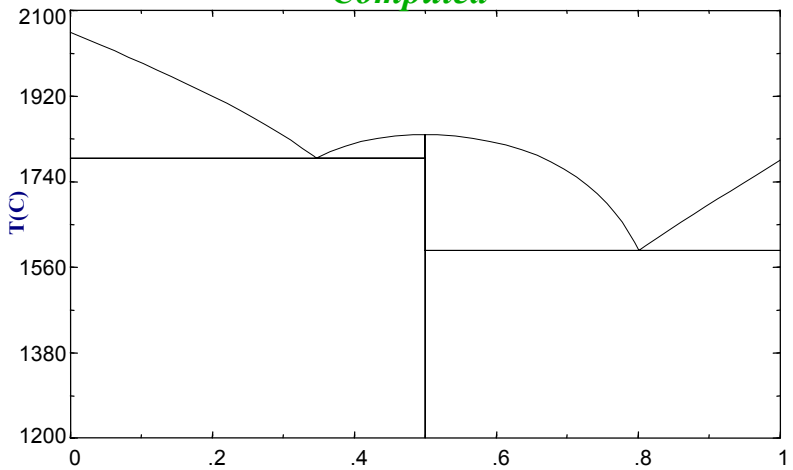

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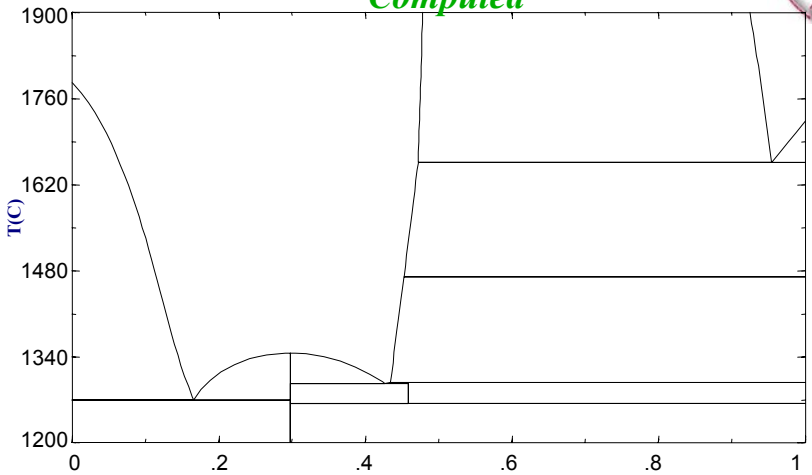

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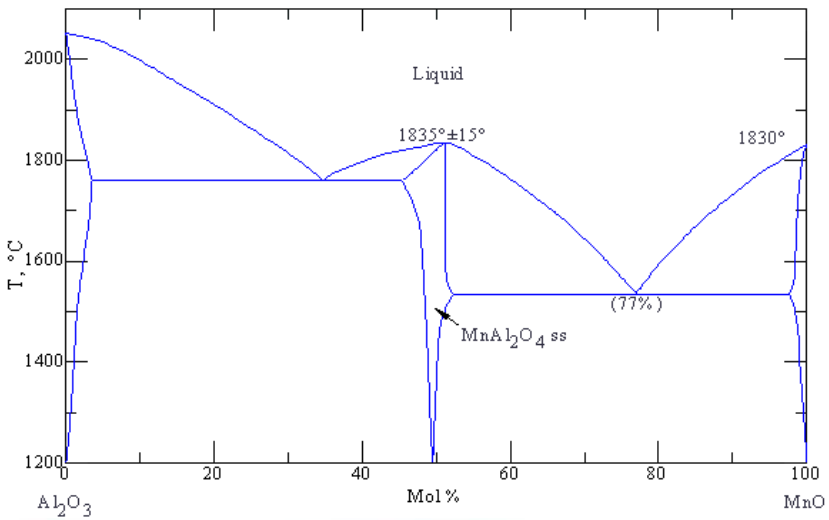

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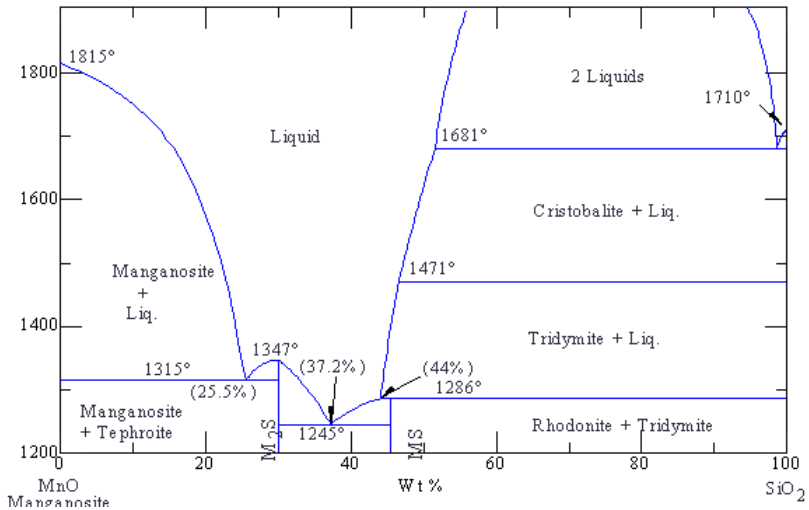

Published and Computed Phase Diagrams for Al_2O_3-NiO and NiO-SiO_2 Show Good Agreement

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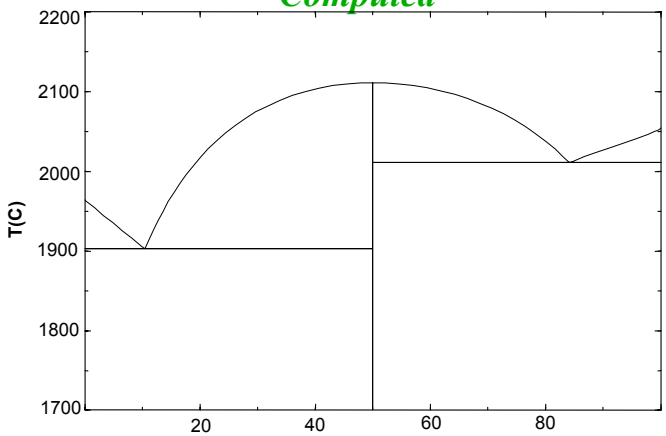

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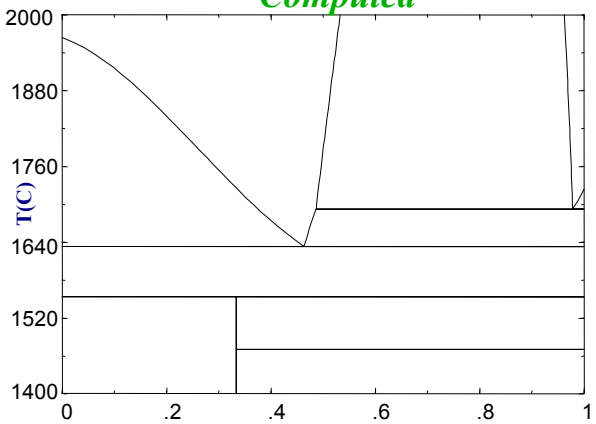

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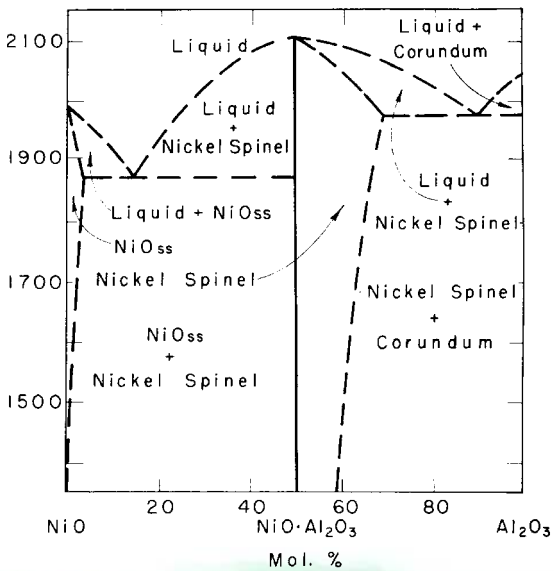

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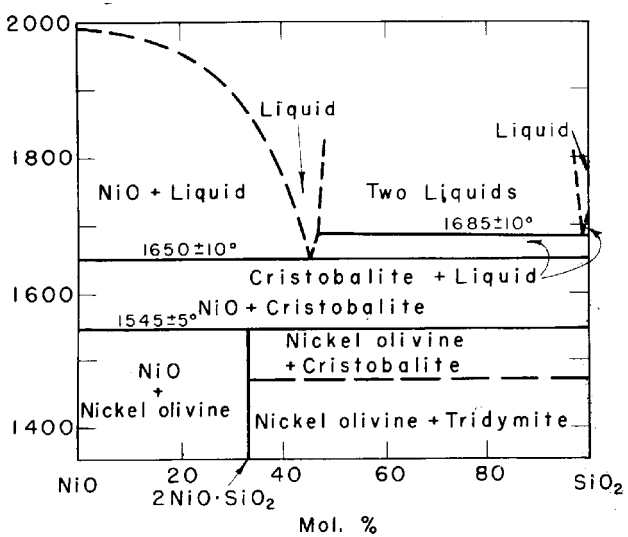
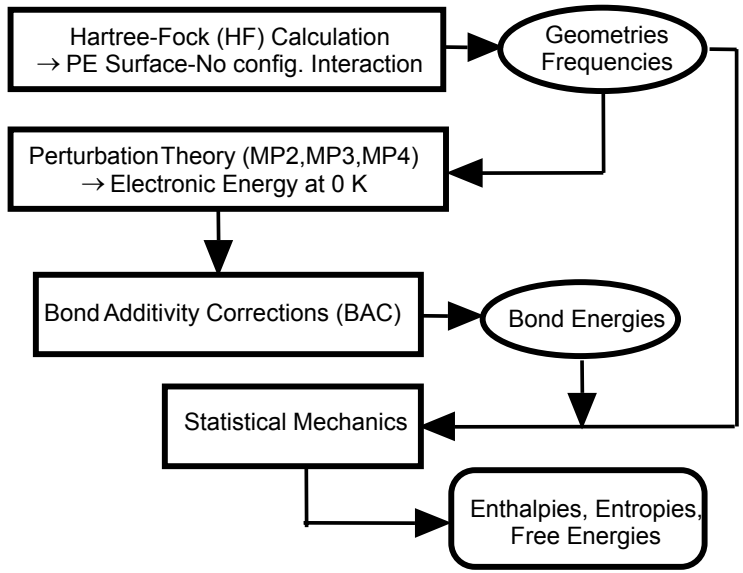


The Bond Additivity Correction (BAC) methods provide accurate gas-phase thermodynamic data

- **Self-consistent set of thermochemical data**
- **Proven accuracy for main-group compounds (B, C, N, O, F, Al, Si, S, Cl, Sn)**
- **Typical accuracy ± 4-8 kcal/mol**



$E_{BAC}(X_i\text{-}X_j) = f_{ij}\, g_{kij}$

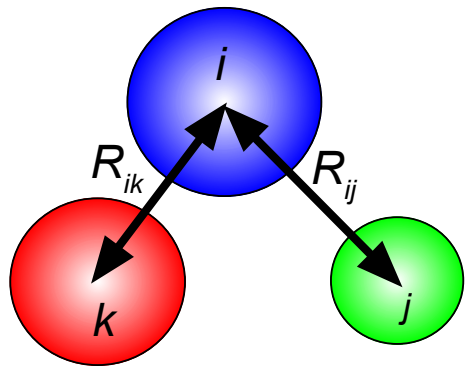
Where:

$f_{ij} = A_{ij} \exp(- a_{ij}R_{ij})$

g_{kij} = accounts for nearest-neighbor interactions

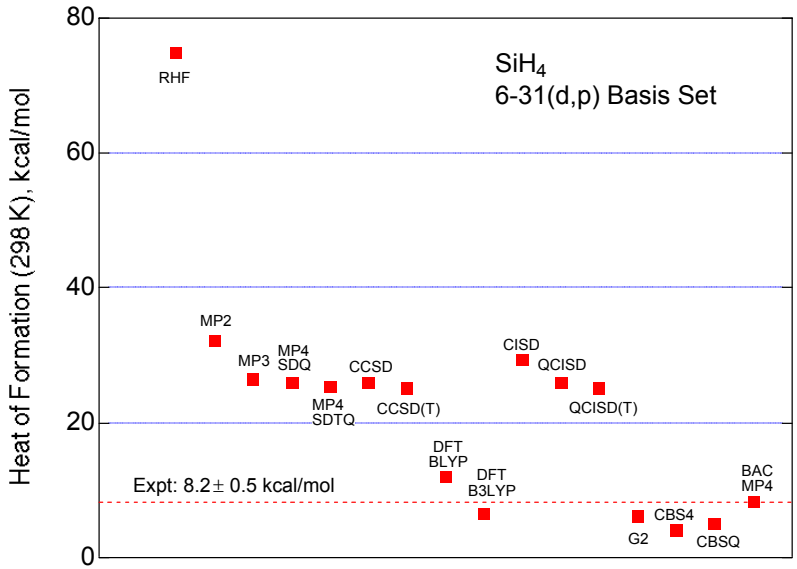
Disadvantages

- **Accurate reference compounds may be required to calibrate method**
- **Becomes computationally impractical for very large molecules (> 8 non-hydrogen atoms)**
- **Applicability to transition metals unclear**



Most *ab initio* methods are not sufficiently accurate to provide useful gas-phase thermochemistry

- **Accurate (± 8-12 kJ/mol) high-temperature data needed to model:**
  - **Corrosion**
  - **Glass manufacturing**
  - **Combustion**
  - **High-temperature materials processing**
- **Systematic errors due to finite basis-set size limits accuracy**
- **Realistic molecules often have > 5 non-hydrogen atoms**
  - **Larger basis sets/higher theory levels rapidly become computationally impractical**
- **Some form of empirical correction is usually required to produce data of sufficient accuracy**
  - **G2 method**
  - **Complete Basis Set method**
  - **Bond Additivity Correction (BAC) method: used in this project**



BAC predictions are in good agreement with established experimental values for main-group species

	ΔH_{f298} (Calc) kJ mol^{-1}	ΔH_{f298} (Obs) kJ mol^{-1}		ΔH_{f298} (Calc) kJ mol^{-1}	ΔH_{f298} (Obs) kJ mol^{-1}
$BHCl_2$	-253.5 ± 4.3	251 ± 4	SiH_2Cl_2	-311.4 ± 4.6	-320.5 ± 12
BH_2Cl	-84.89 ± 4.3	80.8 ± 20	$SiCl_2$	-151.3 ± 15.6	-163.1 ± 10
$B(OH)_3$	-1001 ± 4	-84.1 ± 0.4	SiH_2	271.1 ± 9.2	273.6 ± 5.0
C_2H_4	51.51 ± 4.3	52.3 ± 0.4	$SiHF_3$	-1207.6±5.6	-1200.8±20.9
CH_3	146.0 ± 6.3	146 ± 0.4	$Si(OC_2H_5)_4$	-1328	-1315 ± 4
C_2H_5	120.5 ± 6.7	107.1 ± 5.9	$HSi(CH_3)_3$	-163 ± 4	163.8
NH	364.0 ± 4.6	377 ± 17	$H_2Si{=}CH_2$	170.3 ± 10	154.8 ± 20.1
NH_2	192.9 ± 4.6	190 ± 6	CH_3SiCl_3	-576.6 ± 4.2	569 ± 11
$AlCl_3$	-592± 18	-584.6 ± 2.9	$GaCl_3$	-451.0 ± 5.9	-431.0 ± 8.4
$Al(CH_3)_3$	-53.6 ± 6.8	-56.9 ± 10.5			

The associate species model is being used for oxide liquids and glasses

- Glass thermochemistry is modeled as a solution of constituent compounds
  - e.g., Soda-alumina glass modeled as ideal solution of

    $$Na_2O + AlNaO_2 + Al_2O_3$$

    even though there are at least two more phases in the system
- Great simplification over previous methodologies
  - Treat glass thermochemically as a supercooled liquid
  - No extra parameters that multiply as systems become complex
  - Parameters inherent in species selected for inclusion
  - Allows further simplification by eliminating species that are not "important"
- A modified associate species approach is necessary to accommodate immiscible liquids
  - The presence of two immiscible liquids makes impossible the use of the pure ideal solution/associate species approach
  - Positive interaction parameters are therefore utilized in a model that contains two liquid phases with identical constituents